NASA TT F-486

THE COSINE LAW IN THE KINETIC THEORY OF GASES

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Translation of "Das Cosinusgesetz in der
kinetischen Gastheorie."
Annalen der Physik,
Vol. 48, pp. 1113-1121, 1915.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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THE COSINE LAW IN THE KINETIC THEORY OF GASES

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The validity of the cosine law, developed by Knudsen in earlier experiments on the flow of gases through narrow pipes, is proved for the case of absence of temperature equilibrium in the flow of gases reflected from a surface cooled by liquid oxygen. The experimental method and the apparatus used are described, with equations for the number of mercury molecules reflected from a rigid wall. The validity of the cosine law was demonstrated by the finding that the mercury coating, formed on the condensing surface, was of uniform density no matter whether temperature equilibrium existed or not.

When considering a surface element of an area dS of a solid body located in a gas mass at rest, the number of collisions n′ per second between the gas molecule and the surface element will have a mean value of $n' = \frac{1}{4}N\bar{c}dS$ where N denotes the number of gas molecules in one cubic centimeter, while $\bar{c}$ is the mean velocity of the gas molecules. The knock-on molecules distributed uniformly over each azimuth strike the surface element, and the number of molecules coming from the solid angle dω′ which makes the angle x′ with the normal of the element of area, must be

$$\frac{1}{4\pi} N \bar{c} \cos x' \, d\omega' \, dS \quad \text{or} \quad \frac{1}{\pi} n' \cos x' \, d\omega'.$$

Because of the equilibrium condition, just as large a number of molecules must leave the area element and move into the solid angle dω′ under study. However, this does not unequivocally define the directions into which a single molecule group of n molecules is reflected when all molecules originate in the considered solid angle dω′.

Maxwell (Ref.1) assumed that the direction of reflection of the gas molecules might depend largely on their direction of incidence. He made allowance for this in his calculations by assuming that a fraction f of each unit area reflects the molecules as though they came from a gas mass at rest (absorbed and evaporated gas) while the remainder of the unit area 1 - f would specularly reflect the gas molecules.

From my earlier experiments on the flow of gases through narrow pipes /1114 (Ref.2, 3) I concluded that f = 1 or, in other words, that all n molecules impinging on the area element, coming from the solid angle dω′, must leave this

* Numbers given in the margin indicate pagination in the original foreign text.

element again at velocities uniformly distributed over each azimuth; expressed more accurately, this would mean that the number of molecules with velocity directions within a solid angle $d\omega$ can be written as

$$dn = \frac{1}{\pi} n \cos x \, d\omega.$$

This theorem was designated by me as the "cosine law"; however, the theorem did not gain general recognition since the quantity f was used frequently in papers on the kinetic theory but the question was often raised whether f might have a different value when the gas mass is in temperature equilibrium with the area element dS than when this is not the case. For this reason, I made several experiments to obtain a direct check on the validity of the cosine law.

In these experiments, a method similar to that developed by L.Dunoyer (Ref.4) for sodium vapor was employed; however, it was more convenient to use mercury vapor, partly because of the fact that the vapor pressure of mercury can be measured more accurately. The mercury vapors were ejected from a tube and condensed on a glass wall provided with a small hole. The mercury molecules passed through this orifice like a steam jet since all molecules moved practically in the same direction. This vapor jet struck a solid wall kept at room temperature; the problem was to determine the directions in which the mercury molecules were reflected. This can be determined by permitting the reflected mercury molecules to condense on a glass wall cooled to such a low temperature that only a negligibly small fraction of the molecules striking the cooled wall are re-reflected. That this is actually the case, provided that the condensation wall has the temperature of liquid oxygen, will be demonstrated in a future paper. /1115

In my first experiments on the cosine law, a jet of mercury vapor was allowed to strike a metal surface under an angle of incidence of about 45°. This metal surface had been applied to the center of a spherical glass bulb immersed in liquid oxygen. In several other experiments, the metal surface was replaced by a glass surface and a selenite plate. However, these experiments made in April 1915, will not be discussed further at this point since similar experiments were carried out almost simultaneously by Wood who published a paper on the subject (Ref.5).

Just as reported by Wood, I was able to observe a completely clear and transparent zone along the edge of the mercury deposit, but I did not believe that this zone necessarily was due to a deviation from the cosine law. In special experiments on the reflection of mercury molecules by an intensely cooled glass, a similar zone was observed which became increasingly more narrow in keeping with the subsequent course of the distillation. Since the coating had to have a certain thickness or surface density in order to be detected at all, such a zone must become visible if the cosine law has any validity.

Whereas the mercury molecules, in Wood's and my own experiments, arrived at the reflecting surface at a certain angle of incidence, they were reflected from there in all directions. The coating on the glass bulb formed first at the site where this ball is intersected by the normal to the reflecting surface, after which it spreads uniformly toward all sides; the coating was always thickest at

the point where it was first observed, and the thickness or surface density decreased toward the great circle located in the same plane as the reflecting surface. This does not constitute a contradiction to the cosine law; however, it also does not furnish a reliable proof for its validity. To obtain such a confirmation, the following reasoning was used: /1116

If the validity of the cosine law is to be reliably confirmed by observing the transparency or reflectivity of a mercury coating, the experiment must be so arranged that the cosine law will stipulate that the surface on which the coating is formed has the same surface density throughout. This will be the case if the densifying area represents a spherical surface and the reflecting area forms a portion of the densifying spherical surface.

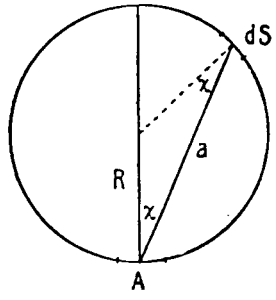

Fig.1

If n molecules originate in an area element A of a spherical surface with a radius R (Fig.1), then the cosine law stipulates that a number of

$$dn = \frac{1}{\pi} n \cos x \, d\omega$$

molecules originate in the solid angle dω. If this solid angle dissects an area element dS from the spherical surface, we have

$$d\omega = \frac{dS \cos x}{a^2}$$

and thus

$$dn = \frac{1}{\pi} n \frac{\cos^2 x}{a^2} dS = \frac{1}{\pi} n \frac{1}{4R^2} dS.$$

The number of molecules on each unit surface of the sphere will be

$$\frac{dn}{dS} = \frac{1}{\pi} n \frac{1}{4R^2}.$$

To this number the surface density ρ of the coating is proportional so that, if an amount by weight of mercury vapor Q is reflected by the area A, we obtain

$$\rho = Q \frac{1}{4\pi R^2}$$

or a density ρ equal to the entire reflected amount divided by the entire surface area of the sphere. Consequently, the surface density ρ is constant if the cosine law is valid; it is quite obvious that any deviation from the cosine law would result in a deviation from the uniform distribution of the mercury over the spherical surface. If the surface element A has a finite size, repeated reflection becomes possible and ρ will be equal to Q divided by the area /1117

of the nonreflecting sector of the spherical surface.

For making this check test, a glass apparatus as shown in Fig.2 was used. The glass bulb A was blown as nearly as possible in a spherical form. The inside diameter was 4.90 cm. The tilted sidearm connects the bulb with the apparatus section in which the mercury vapors are generated. This portion consists of three nested glass tubes C, D, and E, closed at the bottom and fused at the top, as shown in the sketch. The outer tube C is connected to the pump over a sidearm F with ground joint; the space between the inner and middle tube communicates at the top with the closed sidearm G which, in reality, points directly forward rather than - as shown in the sketch - parallel to the tube F. The mercury was placed into this sidearm and, after connecting with the pump, the apparatus was turned such that the /1118 tube G pointed downward. During the pumping process, the mercury in the tube G was extracted by boiling, after which the apparatus was rotated about the ground joint until it reached the position shown in the sketch. This caused the mercury to flow into the interspace between the inner and middle tube Hg. The middle tube was provided with a small hole at the point H, through which the mercury vapors were able to escape into the glass bulb.

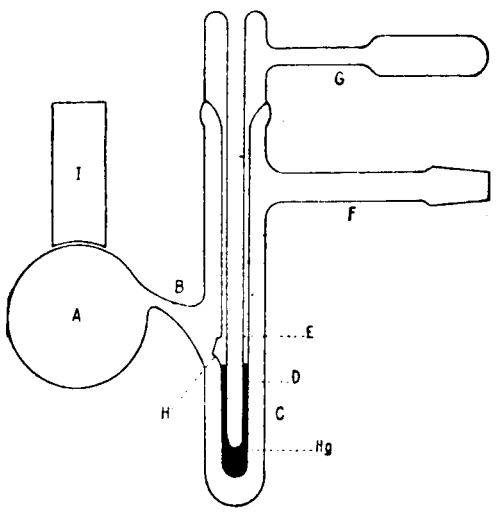

Fig.2

On top of the bulb, a curved segment was left open through which the edge of the hole H could be sighted via the connecting tube B. The curved segment delimits the area of the bulb at the point where the mercury molecules, coming from the orifice H, are able to strike the surface of the bulb; the area was covered by the metal tube I whose metal bottom was milled so that it osculated the glass bulb to which it was cemented with Pizein. The small metal vessel obtained in this manner, of 2 cm outside diameter and 5 cm height, was used for keeping the reflecting glass surface at an elevated temperature during the entire experiment. This vessel was wound with a resistance wire so that it could be heated by electric current and its temperature was checked by means of a thermometer immersed into the vessel in which a small quantity of water was kept. During the experiment the thermometer registered about 30 °C so that the reflecting glass wall presumably had a temperature between 0° and 20° C.

The apparatus was mounted in such a manner that only the uppermost portion of the glass bulb was kept warm whereas the entire remainder of the bulb, the connecting tube B, and a proportional part of the rest of the apparatus was immersed into a 10 cm wide unsilvered vacuum vessel, filled with liquid oxygen. The vacuum vessel could be raised or lowered, which manipulation - together with

frequent replenishing of the liquid oxygen - made it possible to keep the meniscus of the liquid oxygen almost at the level of the metal tube I.

To impart a suitable temperature to the evaporating mercury Hg, a small amount of vaseline was added to the innermost tube which, as shown in the sketch, is open at the top. Into this tube, a small glass rod was inserted whose /1119 bottom was wound with platinum wire to obtain suitable heating by means of an electric current and thus keep the mercury Hg at the prescribed temperature.

In the first experiment with this apparatus, we started with a slight warming of the mercury after the liquid oxygen had been added. During a very brief heating of the mercury, the mercury deposit formed on the tube B became entirely opaque and a mercury coating appeared on the bulb after a few minutes; this coating seemed to appear simultaneously at all points and became increasingly more opàque. It was impossible to detect a structure or a difference in transparency or reflectivity, except along a zone of about 1 mm width surrounding the heating jar J, which remained entirely clear and transparent. After continuing the experiment for about 20 min, the mercury deposit had become so heavy that an electric bulb could just about be discerned through this coating. The experiment was stopped at this point, by disconnecting the heating currents, removing the liquid oxygen, and filling the apparatus with atmospheric air. After the mercury coating had become liquid and the glass bulb had been freed of the hoarfrost formed it was found that the mercury coating exhibited a highly characteristic opalescence which was observed wherever a coating had formed; the diffraction rings, produced by the mercury droplets when a distant electric light was reflected in the glass bulb, had exactly the same appearance over the entire sphere. The last test was made after the glass bulb had been left standing for 24 hrs, so that the mercury droplets had decreased in number and increased in size.

To obtain a quantitative determination of the density of the mercury coating at various points of the glass bulb, the experiment was repeated with more intense heating than before. This experiment again lasted for about 20 min, and the mercury coating reached such a thickness that it became entirely opaque. Again, it was impossible to detect a difference in the various area elements of the glass bulb, either during formation of the coating or after conglomeration of the coating into mercury spherules after termination of the experiment. The glass bulb was then disconnected from the remaining part of the apparatus /1120 and a small mercury droplet was placed into this bulb. The droplet was permitted to run along the side of the bulb to collect the mercury coating, except for three almost circular areas which were oriented and numbered, as shown in Fig.3.

The area No.1 was located at the point where the largest surface density was expected if a portion of the molecules were specularly reflected from the reflecting surface. The spot No.2 was located to one side of the glass bulb while the spot No.3 appeared diametrally opposite the reflecting portion of the spherical surface. The size of the spots was measured, after which they were successively collected by means of another mercury droplet. This made it possible to determine the weight of the mercury at each particular spot. The measurements yielded the following results:

	Area of Spot	Weight of Mercury Coating	Density of Mercury Coating
Spot No.1	5.00 cm^2	0.81 mg	0.162 mg/cm^2
Spot No.2	7.60 cm^2	1.25 mg	0.164 mg/cm^2
Spot No.3	11.24 cm^2	1.62 mg	0.144 mg/cm^2

The difference in these densities is so minor that it can be attributed to errors of observation; in addition, it must a priori be expected that the coating of the spot No.3 has a somewhat smaller thickness than that of the other spots if the cosine law has strict validity, because of the fact that collisions between the incident and reflected mercury molecules must take place in the uppermost portion of the glass bulb and, presumably, produce a greater density at the sites of the spherical surface closest to the point of collision, i.e., a greater surface density than at the bottom where the spot No.3 is located.

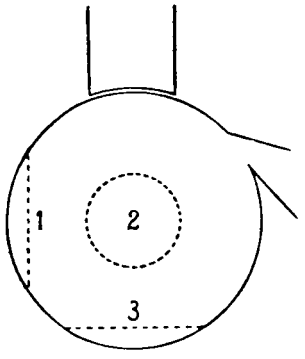

Fig.3

As a result of the experiment, one can conclude that the cosine law here again is /1121 valid with the accuracy obtained in these experiments. The validity of the law, in molecular flow through pipes, had been demonstrated previously for the case in which temperature equilibrium exists between the gas and the reflecting surface. Now, the validity of the law has been proved also for a case in which no temperature equilibrium exists, since the mercury vapors had a temperature of more than 80° C during the experiment, whereas the temperature of the reflecting surface was less than 20° C.

The author wishes to thank the assistants Viggo Andersen and Johannes Olsen for their cooperation. In addition, appreciation is expressed to the Board of Directors of the Carlsbergfond for grants enabling performance of this work.

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Translated for the National Aeronautics and Space Administration by the O.W.Leibiger Research Laboratories, Inc.

NASA-Langley, 1967 — 12 F-486